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LETTER

Organic sulfur: A spatially variable and understudied component of marine organic matter

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Scientific Significance Statement

Organic sulfur is a significant component of cellular material and can be a preferred organic matter source for marine microorganisms. We have limited direct measurements of organic sulfur concentrations and these measurements have not been considered in conjunction with mass spectrometry-based assessments of sulfur-containing organic compounds in seawater. Our results reveal the concentration of organic sulfur was highly variable with depth and latitude in the western Atlantic Ocean. The concentration of organic sulfur was not correlated to the concentration of organic carbon or organic nitrogen. Furthermore, the increased lability of organic sulfur compared to carbon and nitrogen is measurable even during the transit time of deep seawater within a single ocean basin.

Abstract

Sulfur (S) is a major heteroatom in organic matter. This project evaluated spatial variability in the concentration and molecular-level composition of organic sulfur along gradients of depth and latitude. We measured the concentration of total organic sulfur (TOS) directly from whole seawater. Our data reveal high variability in organic sulfur, relative to established variability in total organic carbon or nitrogen. The deep ocean contained significant amounts of organic sulfur, and the concentration of TOS in North Atlantic Deep Water (NADW) decreased with increasing age while total organic carbon remained stable. Analysis of dissolved organic matter extracts by ultrahigh resolution mass spectrometry revealed that 6% of elemental formulas contained sulfur. The sulfur-containing compounds were structurally diverse, and showed higher numbers of sulfur-containing elemental formulas as NADW moved southward. These measurements of organic sulfur in seawater provide the foundation needed to define the factors controlling organic sulfur in the global ocean.

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Author Contribution Statement: KL, GAC, and EBK established the sampling plan. LO and MCKS contributed analytical expertise. KL led the writing of the manuscript with contributions from all authors.

Data Availability Statement: Oceanographic data and metadata from this project are available at the Biological & Chemical Oceanography Data Management Office (BCO-DMO) under project #2204 (https://www.bco-dmo.org/project/2204). The mass spectrometry data and its associated metadata are available from MetaboLights under accession number MTBLS1024 (http://www.ebi.ac.uk/metabolights/MTBLS1024).

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Additional Supporting Information may be found in the online version of this article.

Organic sulfur (S) is a significant component of cellular material (Cuhel et al. 1984), and in marine systems microorganisms preferentially utilize organic sulfur over organic carbon (Matrai and Eppley 1989). Field and laboratory data (Zindler et al. 2013; Durham et al. 2015; Levine et al. 2016) have revealed that microorganisms play a key role in controlling the concentration of organic sulfur compounds. Despite the importance of organic sulfur, there have been few measurements of its concentration in the marine environment. One study at Bermuda Atlantic Time-series Study (BATS) directly measured the concentration of dissolved organic sulfur (DOS) in seawater, though the data are limited to the upper 100 m (Cutter et al. 2004). DOS concentrations ranged from 3 to 689 nM S, with a surface maximum and decrease with depth in the winter (March), but a surface minimum and slight increase with depth in the summer (July–August). Known organic sulfur compounds such as dimethylsulfide (DMS), dimethylsulfoniopropionate (DMSP), dimethylsulfoxide (DMSO), and dimethylsulfoxonium propionate (DMSOP) usually have concentrations in seawater below 20 nM (Zindler et al. 2013; Levine et al. 2016; Tyssebotn et al. 2017; Thume et al. 2018). In the deep ocean, ultrahigh resolution mass spectrometry analysis has revealed an increased presence of elemental formulas that contain sulfur (Kujawinski et al. 2009; Longnecker and Kujawinski 2016). More recently, Ksionzek et al. (2016) indirectly quantified organic sulfur by measuring sulfur concentrations in organic matter extracts and estimated the global pool of organic sulfur in seawater at 6.7 Pg S.

Extraction protocols to remove organic compounds from seawater are necessarily biased. Bulk measurements show that solid-phase extraction resins capture between 20% and 90% of total organic carbon (Dittmar et al. 2008), while extraction efficiencies for known organic sulfur compounds range from 0% to 93%, with low values for DMSP, taurine, and methionine and the highest values for taurocholate and 3-mercaptopropionate (Johnson et al. 2017). Despite these issues, solid-phase extraction is widely used to concentrate dilute organic compounds out of a salty matrix thereby enabling characterization of chemical diversity within seawater and other aqueous solutions.

Our objective was to evaluate spatial variability in the concentration and composition of organic sulfur along gradients of depth and latitude. Given existing measurements of the concentration of particulate organic sulfur in seawater (Matrai and Eppley 1989; Erga et al. 2017), we estimate that ~90% of organic sulfur in our samples will be in the dissolved pool. Concurrently, we characterize the composition of organic sulfur compounds in seawater extracts via mass spectrometry. The combination of these two data sets provides valuable insight into the dynamics of organic sulfur cycling in the western Atlantic Ocean.

Materials and methods

Overview

Seawater samples were collected from the western Atlantic Ocean at five stations along a transect from Uruguay to Barbados (Supporting Information Fig. S1 and Table S1). Water samples were processed to allow direct measurements of the concentration of total organic carbon (TOC), total nitrogen (TN), and total organic sulfur (TOS) along with inorganic nutrients. In addition, organic matter was extracted from seawater using solid phase extraction and analyzed with ultrahigh resolution mass spectrometry. Finally, we used PO4* to define the northern vs. southern component of North Atlantic Deep Water (NADW) as defined by Broecker et al. (1991). Detailed methods are available in the supporting information.

Organic carbon, nitrogen, and sulfur in seawater

High temperature combustion provided the concentration of TOC and TN in whole seawater samples; total organic nitrogen (TON) was obtained by subtracting the concentration of inorganic nitrogen from the TN measurement. TOS was determined as the difference between total sulfur determined by reductive pyrolysis and sulfate, after sulfate concentrations are lowered by pumping water through ion exchange cartridges (Cutter et al. 2004).

Analysis of dissolved organic matter extracts from seawater

During the cruise, dissolved organic matter (DOM) was extracted from seawater using Bond Elut PPL cartridges (Agilent). The organic matter extracts were introduced to the 7 T FT-ICR mass spectrometer by either direct infusion or liquid chromatography. For the direct infusion approach, the organic matter extracts were infused into the mass spectrometer via syringe and elemental formulas were calculated from the resulting mass-to-charge (m/z) values. In the second approach, preseparation using reversed-phase liquid chromatography (RP-LC) and hydrophilic interaction liquid chromatography (HILIC) prior to mass spectrometry analysis was used to characterize the structural diversity of sulfur-containing organic compounds.

Results

Environmental setting

Our samples span from the surface ocean to meters above the seafloor (~5000 m), traverse almost 50° in latitude, and cross biogeochemical provinces and water masses (Supporting Information Fig. S1 and Table S1). The warmest and freshest seawater was found at the surface of the northernmost station (10° North) near the Amazon River plume. In contrast, salinity values exceeding 37°C and a water temperature of 28°C were measured at the surface of 22.5° South, located within the South Atlantic gyre. We used our oxygen and phosphate measurements to serve as the basis to estimate the ages of NADW (Broecker et al. 1991) in our samples. The resulting estimates range from approximately 90 yr (10° North) to 170 yr (3° South), with the 22.5° South and 34.5° South stations actually having younger age, ~120 yr, than those to the north (Supporting Information Table S3).

Table 1. The global inventory of organic sulfur was estimated by combining our data on the concentration of total organic sulfur with Hansell's global inventory of organic carbon in the world's ocean (Hansell et al. 2009). Values for the in situ molar TOC:TOS ratios and total organic sulfur inventory are given as mean values (minimum–maximum). The minimum and maximum values were summed to estimate the global inventory of organic sulfur.

Depth	# of samples	Inventory (Pg C)*	TOC: TOS	Inventory (Pg S)
0–200 m	12	47	387 (108–1472)	0.1 (0–0.4)
200–1000 m	15	138	503 (38–987)	0.3 (0.1–3.6)
>1000 m	17	477	139 (42–311)	3.4 (1.5–11.2)

*Inventory of Pg C comes from Hansell et al. (2009).

Concentrations of organic carbon, nitrogen, and sulfur

TOC concentrations were highest in the surface ocean and decreased with increasing water depth (range: 42 μM to 87 μM; Fig. 1A). The highest concentrations of TOC were measured in the surface of the south Atlantic gyre (22.5° South) and in the vicinity of the Amazon River plume (10° North). TON concentrations varied with depth and sampling station, with values between 0 and 8.7 μM (Fig. 1B). The lowest concentrations of TON were at mid-water depths between 1000 and 2500 m. At all stations except 22.5° South, the TON concentrations were high in the surface and at depth, with mid-water minima. In contrast, at 22.5° South, the highest TON value was measured at 750 m and the lowest values were at 5 m and 2500 m.

The TOS concentrations in whole seawater ranged from below detection (detection limit = 26 nM) to a maximum value of 1275 nM (Fig. 2A, Supporting Information Fig. S2 and Table S2). The highest value is from seawater within the depth range of Antarctic Intermediate Water (AAIW) collected at 10° North. We can group the sampling sites into a station where the TOS concentration showed little variation with depth (3° South), stations where the TOS concentrations increased with depth (38° South, 34.5° South, and 22.5° South), and one station where there was a midwater maximum (10° North). In all of the shallowest (5 m) samples, the TOS concentrations were below detection. There were no significant correlations between the TOS concentrations and temperature, salinity, chlorophyll fluorescence, or the concentrations of inorganic nitrogen or phosphorus (Pearson's correlation coefficient, $p > 0.05$). The TOS concentrations were also not significantly correlated to either TOC or TON concentrations (Fig. S3). The in situ TOC:TOS molar ratios ranged from 38 to 1472, with lower values and a smaller dynamic range below 2000 m (Fig. 2B; Table 1). Water samples collected down to 200 m, on the other hand, showed a large range in TOC:TOS values, ranging from 100 to 1500. In comparison, the average TOC:TON molar ratio was 21 (±14), with a smaller dynamic range throughout the sampling depth range (Supporting Information Fig. S4).

The ratio of organic carbon to organic sulfur in seawater can be used to extrapolate our data to a global estimate of organic sulfur in seawater. To complete this calculation, we relied on the total organic carbon inventory calculated by

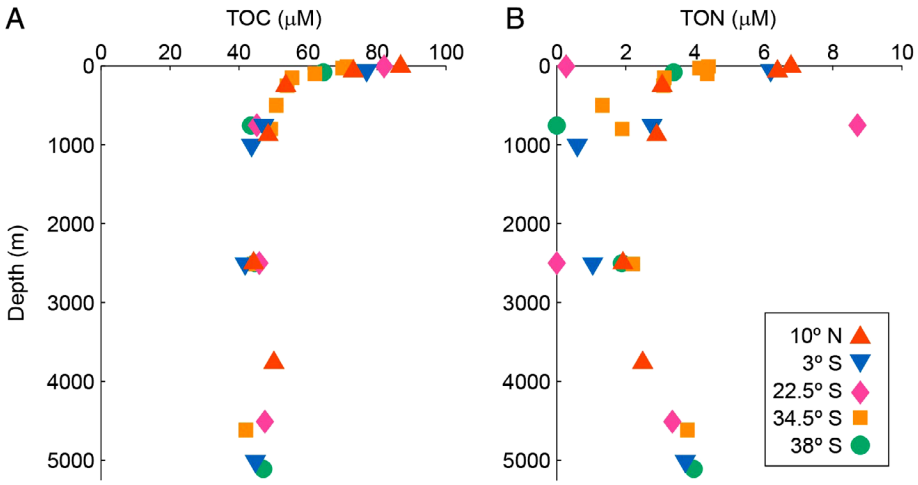

Fig. 1. The concentration of (A) TOC and (B) TON with depth for water samples collected from five stations located in the western Atlantic Ocean.

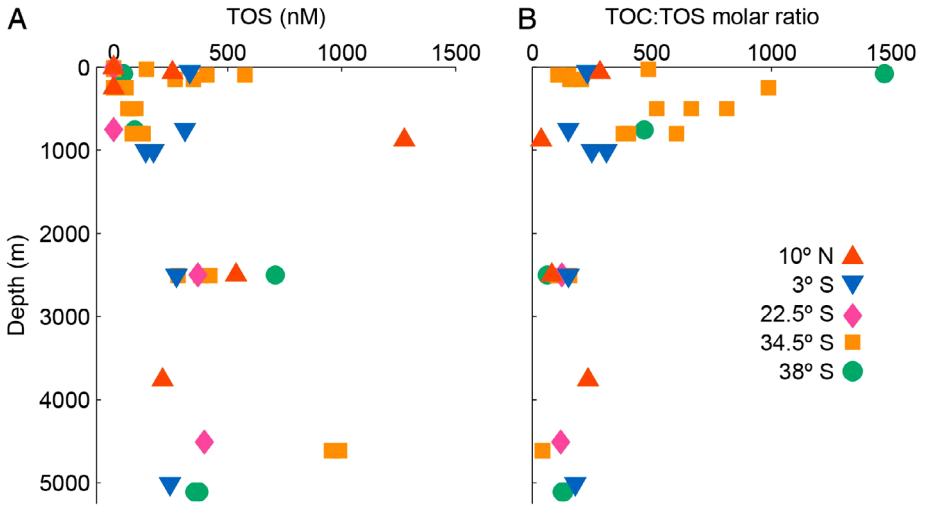

Fig. 2. (A) TOS concentrations, and (B) molar TOC:TOS ratios calculated from TOC and TOS concentrations measured in whole water samples collected from all five stations. The errors for the TOS measurements are given in Supporting Information Table S2 and plotted in Supporting Information Fig. S2 for 34.5°South.

Hansell et al. (2009). Over the full water column, our average organic sulfur inventory is 3.8 Pg S. When the values from the three depth ranges are summed, our measured TOS concentrations scale to an estimated range of organic sulfur in seawater from 1.6 to 15.2 Pg S (Table 1).

Mass spectrometry analysis of DOM extracts

Elemental formulas containing CHO or CHON comprised the majority of elemental formulas in the samples from the western Atlantic Ocean (Supporting Information Fig. S5), and few differences based on sampling depth were observed (Supporting Information Table S4). The elemental formulas containing sulfur were 6% of the *m/z* values, totaling 747 sulfur-containing elemental formulas. Sulfur-containing elemental formulas had a smaller average molecular weight distribution (473.5697 *m/z*) compared to the complete set of elemental formulas (517.6952 *m/z*); this difference was statistically significant (*t*-test, $p << 0.0001$). The sulfur-containing elemental formulas primarily contain CHONS and CHOS, with smaller contributions from CHONSP (Supporting Information Fig. S5). While surface seawater samples had the highest number of unique sulfur-containing elemental formulas, the majority of sulfur-containing elemental formulas were found in all three depth ranges (Fig. S6).

While none of the groups of elemental formulas were correlated to depth or sampling station, the total number of CHONS-containing elemental formulas in NADW (samples from ~2500 m) increased as this water mass moved from north to south (Fig. 3). The number of CHOS and CHONSP elemental formulas were also highest in NADW at the southernmost station. Thus, the diversity of sulfur-containing organic compounds in NADW increased as NADW progressed southward, which corresponds to the increasing estimated age of NADW at the locations sampled in the present project (Supporting Information Table S3).

We used two means to compare the sulfur-containing elemental formulas with the in situ concentrations of TOS in

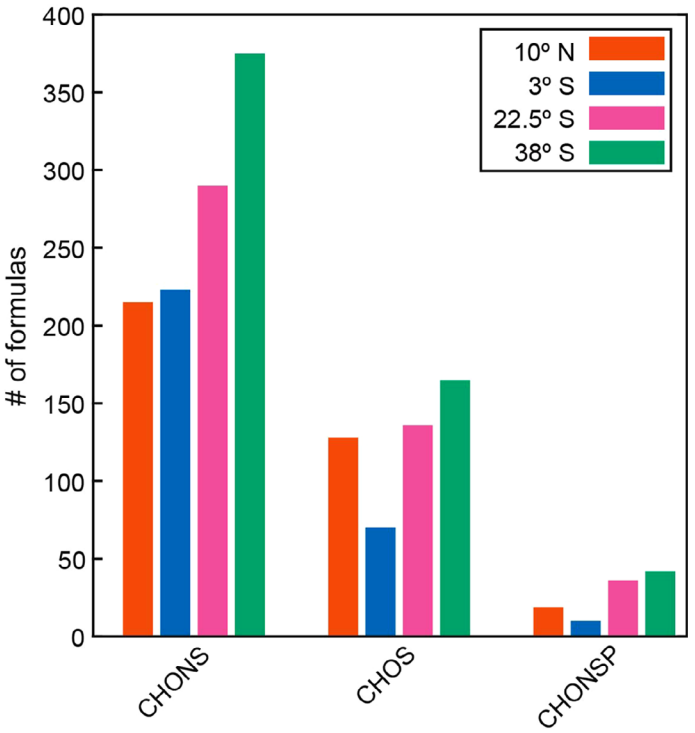

Fig. 3. Sulfur-containing elemental formulas in water samples from North Atlantic Deep Water (NADW, 2500 m) at four stations in the western Atlantic Ocean. The remaining compound groups with sulfur-containing elemental formulas represented less than 0.1% of the elemental formulas in this project.

seawater. In the first comparison, no significant correlation was found between the number or percentage of sulfur-containing elemental formulas and the concentration of TOS in seawater (Pearson's correlation coefficient, $p > 0.05$). Similarly, in the second, no significant correlation was found between the magnitude-weighted sulfur:carbon ratio from the mass spectrometry data and the directly measured TOS concentration (Pearson's correlation coefficient, $p > 0.05$).

Two complementary LC methods provided insight into the structural complexity of the organic sulfur-containing compounds. With RP analysis, the sulfur-containing elemental formulas eluted early in the chromatogram, and again in the period between 5 and 15 min (Supporting Information Fig. S7). Under HILIC analysis, by contrast, the sulfur-containing elemental formulas reached maximum values between 10 and 13 min. With both methods the sulfur-containing elemental formulas were found throughout the chromatogram, which emphasizes the structural diversity of these compounds in organic matter extracts from seawater.

Discussion

Organic sulfur is spatially dynamic in the western Atlantic Ocean

Our cruise track spanned a broad segment of the western Atlantic Ocean and included samples from the surface ocean down to just above the seafloor. There were no significant differences in the flux of particulate organic carbon, measured at 125 m, along this transect (Durkin et al. 2016), and net community production and gross primary production were relatively uniform (Howard et al. 2017). We measured the concentrations of TOC and TON in our samples using well-established protocols. TOC had higher concentrations in the surface ocean and decreased with depth. Measurements of TOC concentrations span the global ocean, and our data are consistent with existing data (Hansell et al. 2009). Although full depth profiles of TON are less common, our data on TON in the water column are consistent with existing depth profiles of organic nitrogen (Ogawa et al. 1999) and data from shallower water depths (<300 m) in the Atlantic Ocean (Torres-Valdés et al. 2009). Concentrations of TOC and TON in the western Atlantic Ocean provide a useful comparison to our organic sulfur data.

In contrast to TOC and TON, the directly measured TOS concentrations were highly variable with depth and latitude, and did not exhibit a consistent pattern along the transect. The concentration of organic sulfur was also not correlated to any of the physical parameters measured in the water column. We considered the possibility that particulate organic sulfur from phytoplankton was a variable source of organic sulfur in our samples, and at station 34.5° South the highest TOS values coincided with the deep chlorophyll maximum. However, this pattern was not observed at other stations. For example, the samples with the highest TOS concentrations were from 876 m at the station near the Amazon River plume (10° North) and replicate samples from 4613 m from 34.5° South, which represent water sampled from AAIW and Antarctic Bottom Water (AABW), respectively. Yet, there were samples from these water masses with lower values, which makes generalizations about organic sulfur in AAIW and AABW challenging.

We found no correlations between either the in situ concentration of TOS and TOC or TON in our data, in contrast with comparisons made with existing DOS data (Ksionzek et al. 2016). The primary difference between our samples and those of Ksionzek et al. (2016) is that we directly measured the concentration of organic sulfur in whole seawater samples while Ksionzek et al. measured the concentration of sulfur in organic matter extracts. The lack of correlation we observed between the concentrations of TOS and TOC indicates that organic matter extracts do not contain representative subsamples of organic matter. This emphasizes the need for direct measurements of organic sulfur concentrations in order to constrain the cycling of organic sulfur in marine ecosystems.

The ratios between TOS and TOC/TON provide insight into how organic sulfur compounds fit within the context of organic matter in our samples. TOC:TOS ratios had a wider range than the TOC:TON ratios. We used the TOC:TOS ratio to estimate an average global organic sulfur inventory of 3.8 Pg S, approximately half the value of 6.7 Pg S reported by Ksionzek et al. (2016). The wide range of our estimated organic sulfur inventory, 1.6 to 15.2 Pg S, is reflective of unknowns in our understanding of organic sulfur in marine ecosystems. Because our data reveal different patterns in TOS concentration at each station, and given the limited data available, caution is warranted when considering our estimate of the global sulfur inventory. However, the underlying data are robust, as they are based on direct measurements of whole seawater.

Organic sulfur compounds in seawater are chemically diverse

Mass spectrometry (MS)-based methods allow us to characterize the complexity of sulfur-containing organic compounds in organic matter extracts. Direct infusion of samples into an ultrahigh resolution mass spectrometer characterizes organic matter based on calculated elemental formulas. The majority of *m/z* values in our samples are CHO- or CHON-containing elemental formulas, consistent with existing characterizations of organic matter in seawater (Kujawinski et al. 2009; Hansman et al. 2015). Of the assigned formulas, those containing sulfur averaged 6%, and the majority of these sulfur-containing formulas were found at all sampling depths. While the surface ocean had the highest number of unique sulfur-containing elemental formulas, these *m/z* values represented a small fraction of the elemental formulas defined by the direct infusion mass spectrometry analysis.

We found no relationship between the mass spectrometry assessment of organic sulfur compounds and the direct measurement of TOS concentrations. The mass spectrometry data

provide the number and percentage of sulfur-containing elemental formulas, and their weighted sulfur:carbon ratios; none of these parameters were correlated to the directly measured TOS concentrations. Solid-phase extraction of sulfur-containing compounds is therefore not proportional to the concentration of organic sulfur in seawater, which presents an analytical challenge because seawater cannot be injected directly into a mass spectrometer. The structural complexity of DOM makes advances into novel methods for extracting and quantifying organic compounds in seawater an interesting challenge for future research.

To gain initial insight into the structural diversity of sulfur-containing organic compounds, we used liquid chromatography coupled to mass spectrometry (LC–MS) to preseparate organic compounds based on their physicochemical properties. Sulfur-containing compounds were ubiquitous across the range of physicochemical properties represented by both chromatography columns. Some of these diverse organic sulfur compounds may be sulfonic acids or thiophenes that have previously been observed in organic matter extracts from seawater samples (Pohlabeln and Dittmar 2015).

Factors controlling variability in organic sulfur

At a given location and depth, the concentration of any organic compound in the ocean is a balance between its in situ production and consumption, and physical transport from elsewhere. The production of DOC during light-driven photosynthetic processes is balanced by consumption through microbial uptake and oxidative respiration (Carlson and Hansell 2015). DOC thus has a near surface maximum and decreases with depth. In contrast, dissolved nutrients such as phosphate are taken up during photosynthesis and released during respiration; phosphate has a surface minimum and increases with depth. As can be seen in Fig. 2, while TOS does not consistently resemble a DOC profile or a nutrient profile, it does include aspects of both. This implies an ongoing source of sulfur from degradation of particles, and subsequent loss via microbial uptake and oxidation. Our TOC:TOS ratios ranged from 38 to 1472, in contrast to a smaller range of particulate organic carbon:sulfur ratios (POC:POS) of 100–200 in surface coastal waters (Matrai and Eppley 1989). The differences between POC:POS and TOC:TOS ratios indicate substantial loss of organic sulfur relative to organic carbon, suggesting that organic sulfur is more labile and reactive than organic carbon.

In addition, we posit that variability in the chemical composition of sinking organic matter could contribute to the spatial variability in TOS concentrations in the water column. During this cruise, the composition of organic matter on sinking particles varied from the compounds observed on suspended particles found at shallower water depths (Johnson et al. 2020). Furthermore, the composition of phytoplankton captured by sediment traps during this cruise varied as a function of latitude (Durkin et al. 2016), which is relevant because the quantity and type of particulate organic sulfur varies across phytoplankton species (Cuhel et al. 1984; Matrai and Keller 1994). Linking the gain or loss of organic sulfur from sinking material will be an important avenue for future research on the factors controlling organic sulfur concentrations in the water column.

In the upper ocean, photochemical processes can also impact organic sulfur compounds, a process that was invoked for the early DOS measurements at BATS (Cutter et al. 2004). Mass spectrometry assessments indicate that organic sulfur-containing elemental formulas exhibit higher losses after irradiation compared to CHO-only elemental formulas (D'Andrilli et al. 2015). Experiments with model organic sulfur compounds reveal that they degrade through secondary reactions in which the organic sulfur compound interacts with photochemically activated chemical species in seawater (Cutter et al. 2004; Mopper et al. 2015). Despite the sunlight, our direct infusion mass spectrometry data revealed the presence of sulfur-containing elemental formulas in the surface ocean, and the sulfur-containing features were structurally diverse. Yet, the concentration of these organic sulfur compounds must be low because TOS concentrations were below detection in water samples shallower than 10 m.

DOM is transported across a latitudinal gradient by ocean currents, such as NADW, flowing southward from the northern Atlantic Ocean towards Antarctica. The time-scale of transport is long enough to observe slow but consistent changes in the concentration and/or composition of organic sulfur over decades. The highest concentrations of TOS within NADW were observed at 38° South followed by the samples from 10° North, while the intermediate stations had the lowest TOS concentrations. Ignoring the southern-most station with its Antarctic influence, TOS decreases with estimated age (537 to 275 nM; Supporting Information Table S3), suggesting removal via respiration/microbial degradation. Significantly, TOC remains relatively constant over this time scale, implying that TOS is a more labile/reactive fraction of organic matter than the bulk material. The early work by Cutter et al. (2004) implied significant photochemical loss in surface waters. Thus, it is likely that presumed high TOS surface waters around Antarctica with a short photochemical oxidation period account for the high TOS concentrations at the 38° S station. However, the diversity of organic sulfur compounds increased along the flow path of NADW, suggesting select organic sulfur compounds are transformed into different organic compounds as NADW flows southward.

Remineralization is one process that may control the cycling and turnover of organic sulfur in the global ocean (Ksionzek et al. 2016; Koch et al. 2017), but mixing of organic sulfur into the deep ocean also plays a role (Dittmar et al. 2017). While our results support the observation that organic sulfur cycles more quickly than organic carbon (Koch et al. 2017), the variability and site-specific differences we measured for TOS concentrations means we cannot evaluate the relative

importance of mixing compared to remineralization. Future assessments in marine systems must include both direct measurements of organic sulfur concentrations along with the ability to estimate biotic and abiotic sources and sinks of organic sulfur in the global ocean.

Our research in the western Atlantic Ocean has revealed that organic sulfur is more spatially dynamic than organic nitrogen and organic carbon, likely due to its short residence time during transport. The measured organic sulfur compounds were structurally diverse, which suggest these compounds may participate in a variety of biogeochemical processes within the marine environment. By directly measuring the concentration of organic sulfur in seawater, we have provided foundational information on organic sulfur concentrations in seawater, and data that are free from the biases associated with the extraction of organic matter from seawater. This information will serve as the basis for defining how organic sulfur is cycled in marine ecosystems.

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